Structural investigations of polar systems using spectroscopic techniques

Synopsis

Submitted to

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For the registration of the topic for

Doctor of Philosophy

in the subject of PHYSICS

(Faculty of Science)

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Introduction:

Probing into the materialistic world reveals very important information about the composition of different materials and different kinds of intermolecular or interatomic interactions within a material. In everyday life, as we encounter a vast variety of substances, it will be more interesting to understand and examine the various properties of these substances by means of some scientific techniques. However the insulating materials fascinate a greater interest. The electrically insulating materials which can be polarized by the application of an external electric field are called as dielectric materials.

The dielectric materials are generally exists in any of the three physical states i.e. solid, liquid and gaseous phase. The molecules by which the dielectric materials made are ofmainlytwo types based on the electrical poles exist inside a molecule. These are polar and non-polar molecules.

In the non-polar molecules the centers of masses of positive and negative charges coincide (e.g. $H_2, O_2, CO_2, CH_4, Benzene, Ethylene, Toluene\ etc.$) while in the polar molecules they are separated by a distance in the order of molecular range. The polar molecules act like small dipoles[1] in the materialslike water, ammonia, ethanol, $SO_2, H_2S\ etc.$ and has a permanent dipole moment. This makes the study of polar systems more interesting and useful for many applications for the betterment of human beings. Hence, for the present work, the polar systems are chosen for the study with the help of spectroscopic techniquessuch as dielectric spectroscopy, FTIR etc.

Literature Review:

The literature survey reveals that there are no constraints on the applications of the polar materials in the daily life. Some of the important applications of polar systems are:in the field of bioengineering[2], to understand various solute and solvent interactions which helps in

designingpharmaceutical products, industries, as solutes and solvents, in electronic devices like batteries, capacitors, super capacitors and many more.

The dielectric relaxation studies of many polar molecules have already been done by many researchers worldwide. From the literature survey, it confirms that the water is a mostly studied polar liquid because of its characteristic behavior[3, 4]. Many other important polar compounds and their mixtures such as 2-methoxyethanol and water, 2-butoxyethanol and water have been studies by Y.S. Joshi and A.C.Kumbharkhane[5, 6]. The dielectric and electrical properties of DMSO and the thermodynamic study of its solution with Erythritol has been done [7, 8]. S.C. Mehrotra has played a vital role in the development of TDR technique in India and has performed the dielectric relaxation studies of many systems.

To do the dielectric spectroscopy of dielectric materialscan be performed by applying frequency domain and time domain techniques. In TDR (Time Domain Refloctometry) technique, a train of fast rising pulses is applied to a sample through a co-axial line. This method at very high frequency range was first developed by H Fellner-Feldegg[9]. S. Mashimoet. al.[10] developed a TDR technique to find complex permittivity of aqueous solutions.

The dielectric parameters of highly polar liquids, diluted polar molecules in non-polar solvents and various electrolytic solutions have been determined by frequency domain and TDR technique. At present, the largely contributing scientists in this research field are D. Bertolini[11],Y. D. Feldman[12-16],U.Kaatze[16-18], S.C.Mehrotra[19-21], R.J.Sengwa[22-25], V.A. Rana [26, 27], A.C. Kumbharkhane[28-33]etc.

In recent times, the Fourier Transform Infrared (FTIR) spectroscopy has been extensively employed by many researchers in material sciences to study the H-Bond interactions.But it can’t identify the exact order of complexes formed as a result of various interactions. This if one of the disadvantage about this technique, hence some theoretical calculations needed to be done to extract more precise information on the nature of complexes formed in a mixture of compounds[34-43]. DFT (Density-Functional Theory) calculations are such theoretical calculations depending on quantum mechanics[44].

Objectives of research hypothesis:

- Measuring the complex permittivity of interested polar liquids and their binary mixtures with different types of solvents very precisely using TDR technique.
- Determining the relaxation time, static dielectric permittivity, dielectric loss and high frequency dielectric permittivity by using suitable mathematical models.
- To measure the refractive indices of associated liquid compounds and their binary mixtures.
- To study the molecular interactions and hydrogen bonding in the associated liquid compounds and their binary mixtures using various parameters like Kirkwood correlation factor, Bruggman factor, thermodynamic parameters, excess parameters,their responses to IR radiation etc.
- Confirming the formation of dimers due to parallel or antiparallel alignments of molecules usingFTIR technique.

Methodology to be adopted:

The TDR technique proved very useful to investigate the molecular structures and their dynamics. In this technique a fast rising step voltage is propagated in a sample through an ideal coaxial line of 50 Ω characteristic impedance. The pulse reflected from the sample is captured and compared with the shape of the incident pulse using digital serial analyzer.This technique is being used for the determination of complex permittivity of different kinds of 'polar' molecules at various frequency ranges. This may be anticipated to produce better dielectric relaxation parameters in this frequency range because the permittivity spectra are obtained by a single measurement.

To determine the electrical and dielectric properties of the selected systems 'capacitive measurement method' in frequency domain can be used at lower frequencies from few Hz to some MHz. The capacitances of the Liquid Dielectric Test Fixture will be measured with and without samples. The Test Fixture correction usingshort compensation shall be considered to cancel the stray capacitance during the determination of dielectric constant values.

The FTIR is a technique used to obtain an Infrared Spectrum of absorption or emission of a solid, a liquid or a gas. FTIR spectrometer simultaneously collects high resolution spectral data over a wide spectral range.

The term Fourier-Transform Infrared Spectroscopy originates from the fact that the mathematical process Fourier Transform is required to convert the raw data into the actual spectrum. In this technique the spectrometer shines a beam containing many frequencies of light at once and measures how much of that light is absorbed by the sample. After then, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is rapidly repeated many times over a short time span. The raw data obtained is manipulated through computer processing to obtain the desired results.

Importance of study/ society applications:

The following scientists are doing research in this field at national and international level:

International Status:

1. N. Shiyanshiki, University of Tokyo, Tokyo, Japan
2. S. Yagihara, University of Tokyo, Tokyo, Japan
3. S. Sudo, Dept. of Physics, Tokyo City Univ. Tamazutsumi, Setagaya, Tokyo, Japan
4. A. Cataldo, Universita di Lecce, via Monteroni, 73100 Lecce, Italy
5. U. Kaatze, DrittesPhysikalischesInstitut Georg-August-Universitat Gottingen, Germany.
6. Y.D. Feldman, Department of Applied Physics, Hebrew University of Jerusalem, Jerusalem, Israel.

National Status:

1. S.C. Mehrotra, Dr. BAMU, Aurangabad, Maharashtra
2. R.J. Sengwa, JNV University, Jodhpur, Rajasthan
3. A.C. Kumbharkhane, SRTM University, Nanded, Maharashtra
4. V.A. Rana, Gujarat Univirsity, Ahmedabad, Gujarat

Significance of the study:

The dielectric relaxation measurements of liquid solutions impact largely on the fundamental study of materials. The present study is devoted to dielectric relaxation measurement of polar liquids using TDR technique from few Hz to 50GHz as well as the FTIR spectroscopy of the same.

From this study, one can understand the orientation and hydrogen bonding interactions of polar molecules through solute-solvent interactions. The proposed study may help to improve the applicability of many polar liquid compounds in various fields such as electrical and electronics, pharmaceuticals, bioengineering, industries etc.

Work plan/ formulation and structure of study:

- **First Year:** To prepare the theoretical background of research problem and detailed literature survey. Then choosing the appropriate polar liquids for the dielectric measurements.

- **Second Year:** To study the dielectric dispersion of selected polar liquids at different frequencies and perform FTIR spectroscopy. To evaluate the dielectric properties such as static dielectric permittivity, relaxation time, dielectric permittivity at high frequency and structural information of these systems. To measure the refractive indices and densities of these liquids.

- **Third Year:** Dielectric and FDR information extracted from data analysis of these systems will be used further for interpretations of molecular behavior. These interpretations will be published by writing research papers or presenting the work in conference/seminars. Finally, write up thesis and complete the research work.

References:

[1] J.N. Israelachvili, Chapter-4, book: Intermolecular and surface forces, Edition 3 revised, Academic Press, ISBN V 978-0-12-375182-9, (2011).

[2] B.D. Ratner, A.S. Hoffman, S.L. Mcarthur, chapter-1.4.2, Biomaterials Science: An introduction to materials in medicine, ISBN 0-12-582463-7 (pp.487-505).

[3] G. Salvetti, Hydrogen-Bonded Liquids, ISBN 978-94-010-5445-4 (pp.369-380), (1991).

[4] S.Yagihara, Conference:13th ISEMA, 2021.

[5] Y.S. Joshi, A.C.Kumbharkhane, J. Mol. Liq. 161 (3) (2021) 120-124.

[6] Y.S. Joshi, A.C.Kumbharkhane, Fluid Ph. Equilibria 317(2012) 96-101.

[7] Y.S. Joshi, K.S.Kanse, A.C.Kumbharkhane, V.A. Rana, SRTMU's Res. J. of Science Vol. no. 3 (2014) 2277-8594.

[8] D.N.Rander, M.A. Joshi, Y.S. Joshi, K.S.Kanse, A.C.Kumbharkhane, Scholars Research Library Archives of Phys. Research 7(3)(2016)1-8.

[9] H. Fellner-Feldegg, J. Phys. Chem. 73 (1969) 616.

[10] S. Mashimo, T. Umehara, T. Ota, S. Kuwabara, N.Shinyashiki and S. Yagihara, J. Mol. Liq. 36 (1987) 135.

[11] D. Bertolini, M.Cassettari, G. Salvetti, E. Tombari, Veronesi, Rev. Sci. Instrum., 61 (1990) 450.

[12] V. Raicu, Y.D. Feldman, in book: Dielectric Relaxation in Biological Systems Physical Principles, Methods, and Applications, ISBN: 978–0–19–968651–3

[13] A. Puzenko, P.B. Ishai, Y.D. Feldman, Phys. Rev. Lett., PRL 105 (2010) 037601.

[14] I. Popov, P.B. Ishai, A. Khamzin, Y.D. Feldman, Phys. Chem. Chem. Phys., 18 (20) (2016) pp. 13941-13953.

[15] L. Latypova, A. Puzenko, A. Bogdanova, Y.D. Feldman, 13th International Conference on Electromagnetic Wave Interaction with Water and Moist Substances (ISEMA), 2021.

[16] U. Kaatze, Y.D. Feldman, Meas. Sci. Technol. 17 (2006) R17–R35.

[17] U. Kaatze, J. Mol. Liq., 315 (2020) 113788.

[18] U. Kaatze, “Water: Why Is it So Special?”, IEEE2018.

[19] R.J. Sengwa, R. Chaudhary, S.C. Mehrotra, Mol. Phys., 99 (21) (2001) 1805-1812.

[20] S.C. Mehrotra, V.A. Rana, A.D. Vyas, J. Mol. Liq., 102/1–3 (2002) 379–391.

[21] B.G. Lone, S.C. Mehrotra et. al., J. Mol. Liq., 141 (2008) 47–53.

[22] R.J. Sengwa, J. Mol. Liq., 108(1-3) (2003) 47–60.

[23] R.J. Sengwa, S. Sankhla, N. Shinyashiki, J. Solution Chem., 37 (2008) 137–153.

[24] R.J. Sengwa, S. Choudhary, P.Dhatarwal, J. Mol. Liq., 225 (2017) 42–49.

[25] S. Choudhary, P. Dhatarwal, R.J. Sengwa, J. Mol. Liq., 231 (2017) 491–498.

[26] V.A. Rana, V.A. Pandit,J. Mol. Liq., (2020) 113673.

[27]N.S. Shah, P.S. Shah, V.A. Rana, Ionics, 21(12) (2015) 3217–3222.

[28] S.S. Kadam, K.S. Kanse, Y.S. Joshi, D.N. Rander, A.C. Kumbharkhane, Indian J. Phys., 92(1-3) (2018) 1-6.

[29]A.Mohan, M.Malathi, S.S. Shaikh, A.C. Kumbharkhane, J. Solution Chem., 45(2) (2016) 221–234.

[30] D.N. Rander, Y.S. Joshi, K.S. Kanse, A.C. Kumbharkhane, Indian J. Phys., 90(1) (2016) 67–72.

[31] D.G. rathod, D.N. Rander, K.S. Kanse, Y.S. Joshi, A.C. Kumbharkhane, Journal of the Maharaja Sayajirao University of Baroda, ISSN: 0025-0422, Volume-55, No.2 (2021).

[32] D.G. Rathod, D.N. Rander, K.S. Kanse, Y.S. Joshi, A.C. Kumbharkhane, Carbohydr. Res., 507 (2021) 108375.

[33] P.A. Bhadane, D.N. Rander, K.S. Kanse, Y.S. Joshi, A.C. Kumbharkhane, Phys. Chem. Liq., (2020) 1-9.

[34] P. Dineshkumar, R. Sahana, R. Shanmugam, A. Elangovan, R.K. Sankaranarayanan, A.C. Kumbharkhane, Y.S. Joshi, G. Arivazhagan, Chem. Phys. Lett., 787 (2022) 139272.

[35] G. Arivazhagan, A. Elangovan, R. Shanmugam, R. Vijayalakshmi, P.P. Kannan,Chem. Phys. Lett., 627 (2015) 101.

[36] A. Elangovan, R. Shanmugam, G. Arivazhagan, A. Mahendraprabu,N.K. Karthick, Chem. Phys. Lett. 639 (2015) 161.

[37] N.K. Karthick, G. Arivazhagan, A.C. Kumbharkhane, Y.S. Joshi, P.P. Kannan, J. Mol. Struct., 1108 (2016) 203.

[38] G. Arivazhagan, R. Shanmugam, A. Elangovan, Spectrochim. Acta, Part A 105(2013) 102.

[39] N.K. Karthick, P.P. Kannan, A. Mahendraprabu, G. Arivazhagan, N. Suganya, J. Mol. Liq. 232 (2017) 147.

[40] A. Mahendraprabu, A.C. Kumbharkhane, Y.S. Joshi, S.S. Shaikh, P.P. Kannan, N.K. Karthick, G. Arivazhagan, J. Mol. Struct. 1136 (2017) 303.

[41] N.K. Karthich, G. Arivazhagan, P.P. Kannan, A.C. Kumbharkhane, Y.S. Joshi, J. Mol. Struct., 1192 (2019) 208-216

[42] G. Arivazhagan, A. Elangovan, R. Shanmugam, R. Vijayalakshmi, P.P. Kannan, Chem. Phys. Lett. 627 (2015) 101.

[43] A. Elangovan, R. Shanmugam, G. Arivazhagan, A. Mahendraprabu, N.K. Karthick, Chem. Phys. Lett. 639 (2015) 161.

[44] T. van Mourik, R.J. Gdanitz, J. Chem. Phys., 116 (2002) 9620.

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